Optically Active Phosphophosphidites

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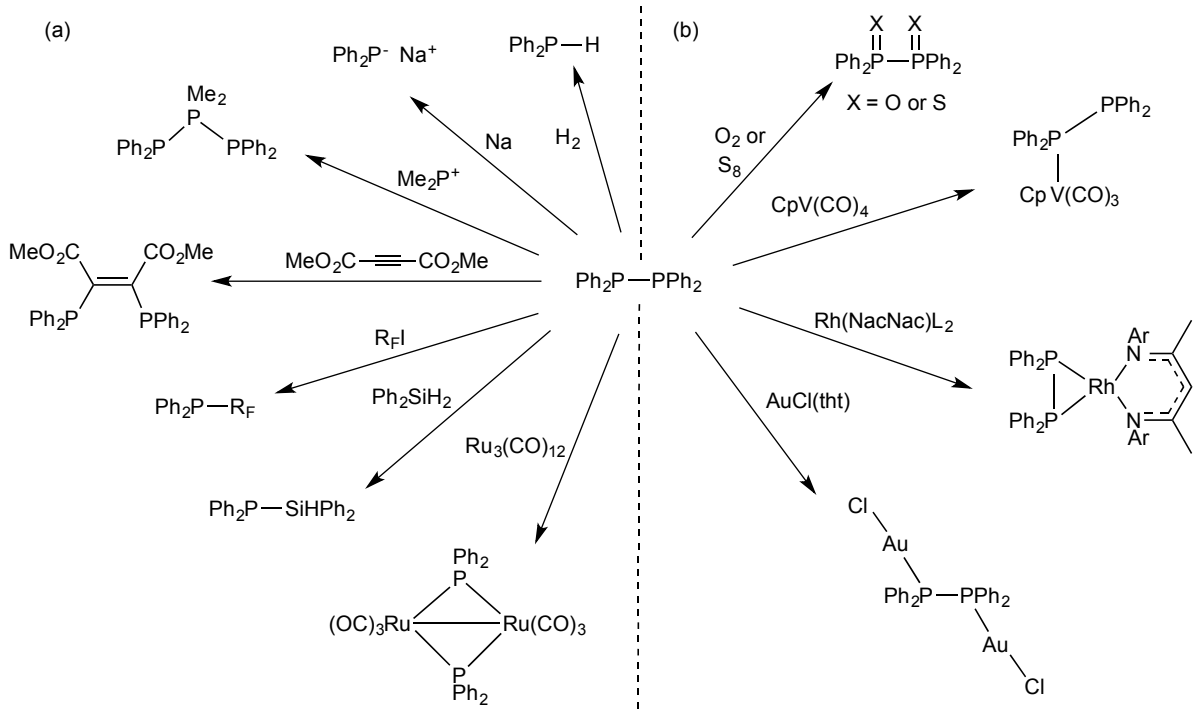
Abstract: Phosphophosphidites of the type R_2P–P(binol) (where binol = the dianion of *S*-1,1'-bi-2-naphthol) are the phosphorus analogues of the ubiquitous phosphoramidites, R_2N–P(binol) and are readily accessed by the chlorosilane elimination reaction between R_2P–$SiMe_3$ and Cl–P(binol). The crystal structure of $^{i}Pr_2P$–P(binol) (**1**) has been determined and shows a P–P bond length in the normal range. The solution reactions of **1** have been investigated, principally by ^{31}P which has revealed that: (a) in contrast to the phosphoramidites, **1** is extremely moisture sensitive; (b) the P–P bond in **1** is cleaved upon reaction with H_2O, MeOH or mesitol; (c) the P–O bonds in **1** are cleaved upon reaction with pyrollidine; (d) the integrity of **1** is retained upon coordination to BH_3 or Mo(0). The crystal structure of *cis*-$[Mo(CO)_4(\mathbf{1})_2]$ shows that **1** is bound to the Mo at the P(binol) site and the ν_{CO} of 2032 cm^{-1} indicates that **1** has similar ligand properties to a phosphonite.

Introduction

Homodiphosphanes $Z_2P–PZ_2$ are amongst the simplest catenated phosphorus species and are known with a wide variety of Z substituents including H, halogen, OR, NR_2, fluorocarbyl and hydrocarbyl.[1,2,3,4] The chemistry of diphosphanes is dominated by P–P cleavage reactions, as illustrated in Scheme 1(a) which shows representative examples of the chemistry of the most studied diphosphane, $Ph_2P–PPh_2$.[5,6,7,8,9,10] There are also reactions of $Ph_2P–PPh_2$ in which the P–P bond is retained (see Scheme 1(b) for examples), notably in its chalcogenation[11] and in its coordination complexes where it can act as a terminal,[12] chelating[5] or bridging[13] ligand.



Scheme 1 Illustration of the array of reactions undergone by $Ph_2P–PPh_2$ involving (a) P–P bond cleavage or (b) P–P bond retention

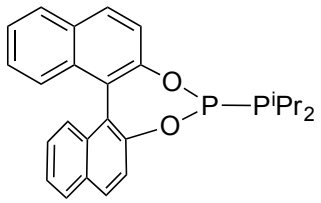
Heterodiphosphanes, $Z_2P–PY_2$ where Y and Z are different hydrocarbyl, fluorocarbyl or P–N containing groups are well known.[1,3,14,15,16,17] The inherently dipolar nature of heterodiphosphanes can lead to kinetic lability with respect to P–P cleavage reactions (vide

infra). In some cases, metathesis of the type shown in Eq. 1 is observed in heterodiphosphanes.[3,8]

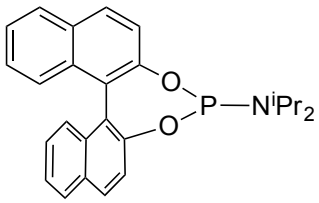
$$Z_2P{-}PY_2 \rightleftharpoons Z_2P{-}PZ_2 + Y_2P{-}PY_2 \qquad \text{Eq 1}$$

Phosphophosphidites, $(R'O)_2P{-}PR_2$ are examples of heterodiphosphanes but their chemistry has been little studied.[18,19,20] They are the phosphorus congeners of the well-known phosphoramidites $(R'O)_2P{-}NR_2$ which have found important applications in a variety of homogeneous metal-catalysed asymmetric reactions[21,22] and are used extensively as intermediates in oligonucleotide synthesis.[23] Here we report the synthesis and properties of the optically active 1,1'-bi-2-naphthol-derived phosphophosphidite **1** and related species and draw comparisons with the phosphoramidite analogue **A**.[24]

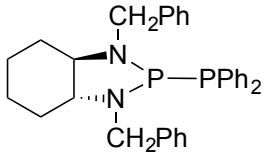
Diphosphane **1** has features in common with the previously reported[17] diphosphane **B**. They are both rare examples of optically active diphosphanes and both contain phosphacycles, albeit of different ring sizes and with different heteroatoms.



1



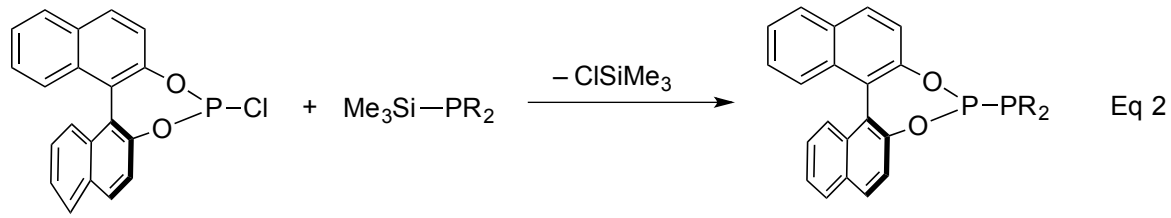
A



B

Results and Discussion

The addition of silylphosphine $^{i}Pr_2P–SiMe_3$ to the phosphochloridite (*S*-binol)P–Cl gave a single product which was characterised as the phosphophosphidite **1** (Eq 2) by a combination of ^{31}P, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (see Experimental for the data). The solution structure of **1** was based on its characteristic ^{31}P NMR spectrum which showed two doublets at δ(P) = +260.1 and -0.5 ppm with a large $^{1}J(PP)$ = 267 Hz.



Eq 2

1 R = ^{i}Pr
2 R = Cy
3 R = ^{t}Bu
4 PR_2 = P
5 R = Ph

Crystals of **1** slowly formed from the oil that is initially isolated from the reaction mixture. The X-ray crystal structure of these crystals confirmed the molecular structure (Figure 1); the P–P bond length in **1** falls within the normal range.[3,25,26] The conformations about the P–P bond that are adopted in diphosphanes have previously been discussed[26] and recently been systematically categorised[3] as staggered or eclipsed with subcategories based on the relative positions of the lone pair as *anti/gauche* or *anticlinal/synclinal*. Using these descriptors, **1** adopts an eclipsed/*anticlinal* conformation. A space-filling model of **1** (see SI) shows that the P atom of the $P^{i}Pr_2$ moiety is less accessible than the P atom of the P(binol) moiety; this may be significant in rationalising the relative Lewis basicities of the two sites (vide infra).

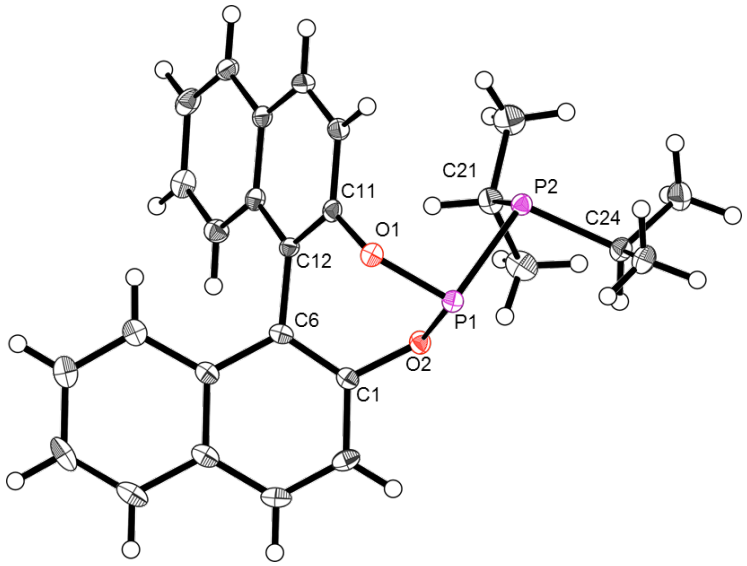


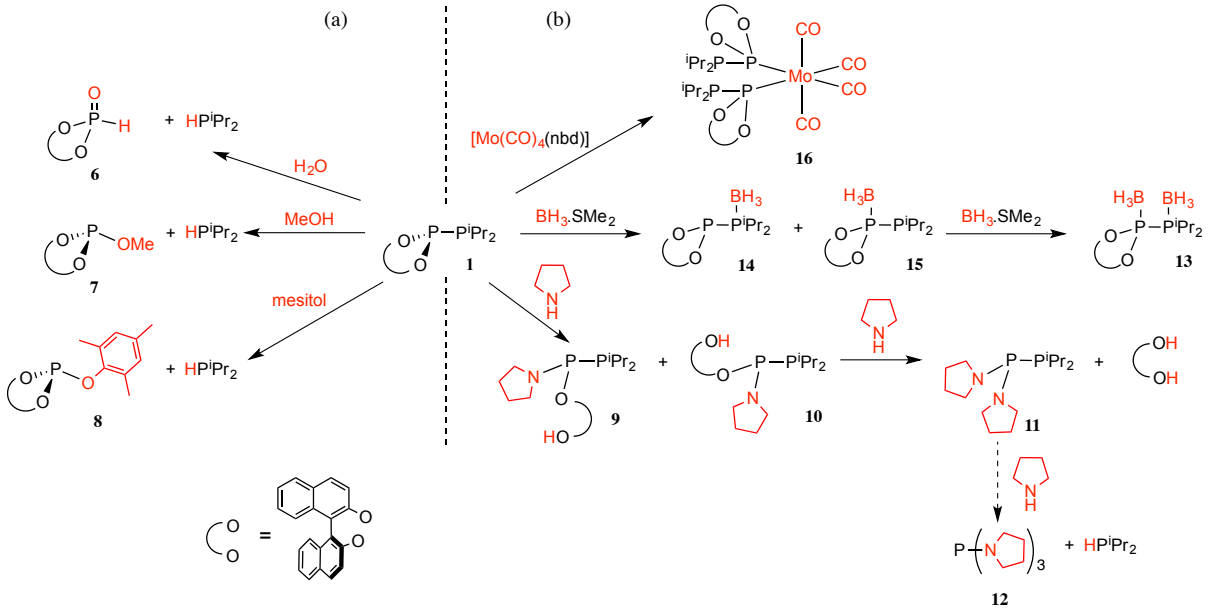
Figure 1. X-ray crystal structure of **1**. Selected bond lengths (Å) and angles (°) for **1**: P1-P2 2.2358(8), P1-O1 1.6625(17), P1-O2 1.6644(17), P2-C21 1.875(3), P2-C24 1.869(2), O1-P1-P2 98.78, O2-P1-P2 101.26(6), O1-P1-O2 98.94(9), C21-P2-P1 105.34(8), C24-P2-P1 99.57(8), C21-P2-C24 106.74(12).

The chlorosilane elimination reactions between (binol)P–Cl and other $R_2P–SiMe_3$ (R = alkyl) proceed efficiently to produce **2-4** (Eq. 2) which have been characterised by a combination of ^{31}P, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The reaction between (binol)P–Cl and $Ph_2P–SiMe_3$ produced the expected phosphophosphidite **5** but only in *ca.* 90% purity; two P-containing by-products were present (5% each), one of which was identified as $Ph_2P–PPh_2$ [δ(P) = -14.3] which is consistent with metathesis of the type shown in Eq 1 taking place and led to the other product (with δ(P) = +209.6) being tentatively assigned to the previously unknown diphosphane $P_2(binol)_4$; the mass spectrum of the product mixture supported the presence of **5** and the two derived homodiphosphanes (see Experimental for the data).

Compound **1** was prepared in sufficient quantities for the chemistry of this phosphophosphidite to be further investigated. Solutions of **1**, in the absence of water, are stable for weeks according to ^{31}P NMR spectroscopy.

Reactions of phosphophosphidite 1 with protic reagents

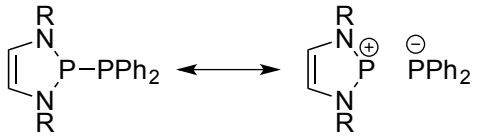
The reactions of **1** with ROH (R = H, Me, Mesityl) are shown in Scheme 2(a); the progress of these reactions has been monitored by ^{31}P NMR spectroscopy and the products identified by comparison with the literature ^{31}P NMR data. In each reaction, one of the products was $^{i}Pr_2PH$ [δ(P) = -15.5 ppm, ^{1}J(PH) = 164 Hz].[27] The reaction of **1** with 1 equiv. of water occurred rapidly and quantitatively to give **6** [δ(P) = +14.5 ppm, ^{1}J(PH) = 737 Hz].[28] The acute sensitivity of **1** to even traces of water contrasts sharply with the remarkable water-stability of the analogous phosphoramidite **I**.[24] The reactions of **1** with dry methanol or mesitol were also rapid and produced the phosphites **7** [δ(P) = +138 ppm][29] and **8** [δ(P) = +149 ppm][30] respectively.



Scheme 2 Reactions undergone by phosphophosphidite **1** involving (a) P–P bond cleavage or (b) P–P bond retention

The high reactivity of P–P bond in **1** towards ROH is reminiscent of the reactivity of the P–P bond in Gudat's compound **C**.[14] The lability of **C** has been associated with its long P–P bond length (2.334(1) Å) and its ionicity which stems from the stability of the N-heterocyclic phosphenium moiety (see Scheme 3). However, the P–P bond length in **1** is much shorter

(~0.1 Å) than in **C**, indicating that, while both **1** and **C** have highly polar P–P bonds, the details of the bonding in each are significantly different.



C

Scheme 3. Canonical forms of diphosphane **C**.[14]

In the hope of producing phosphoramidite **A**, $^{i}Pr_2NH$ was added to **1** but no reaction took place even after 7 days under ambient conditions. However, when **1** was dissolved in pyrollidine, a slow reaction does take place but not to give a phosphoramidite. Instead, a mixture of products evolved over a period of 40 h (see SI for the spectra). Initially, two P–P bonded species are formed which have similar ^{31}P NMR parameters and are assigned to the mixture of diastereoisomers **9** and **10** which would be expected from the monoaminolysis of **1** (Scheme 2). Subsequently, another P–P bonded species is detected whose ^{31}P NMR parameters [δ(P) = +86.0 and -28.0, ^{1}J(PH) = 181 Hz] are compatible with a $R_2P–P(NR_2)_2$ species[3] and therefore it is assigned the structure **11**. In addition, small amounts (< 5% of the total ^{31}P NMR signal intensity) of $HP^{i}Pr_2$ and tris(pyrollidinyl)phosphine (**12**) [δ(P) = +105.0][31] were also detected; these ultimate products represent complete aminolysis of **1** accompanied by P–P cleavage (Scheme 2).

Donor properties of phosphophosphidite 1

Addition of 2 equivalents of $BH_3.SMe_2$ to compound **1** gave the bis(borane) adduct **13** (Scheme 2) which has been characterised by ^{31}P, ^{11}B, ^{13}C and ^{1}H NMR spectroscopy and mass spectrometry. Compared to **1**, in the borane adduct **13**, the J(PP) is reduced by 57 Hz and the δ(P) values indicate that the $P^{i}Pr_2$ moiety is deshielded by *ca.* +50 ppm while the P(binolate) moiety is shielded by a remarkable *ca.* -80 ppm. When 1 equivalent of $BH_3.SMe_2$ was added to compound **1**, the ^{31}P NMR spectrum showed the presence of four species in approximately equal amounts: starting material **1** and its bis(borane) adduct **13** along with 2

new species which are assigned to the monoborane adducts **14** and **15** (Scheme 2 and SI for the ^{31}P NMR spectra). We had anticipated that the BH_3 would bind selectively to the more electron-rich P^iPr_2 site of **1**[32] but the experimental results suggest that affinities for BH_3 of the two component P-moieties in **1** are similar. One interpretation of this observation is in terms of the stereoelectronic availability of the lone pairs[33] at the two P sites in **1**: the P of the P^iPr_2 should be more electron-rich but this is balanced by it being sterically less accessible than the P of the P(binol).

Finally, addition of 2 equivalents of **1** to $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) at ambient temperature gave the *cis*-complex **16** (Scheme 2) as shown by a combination of ^{31}P and ^{1}H NMR and IR spectroscopy. Crystals suitable for X-ray crystallography were grown from CH_2Cl_2 / hexane and the structure shown in Figure 2 confirms that the ligand **1** is bound to the Mo at the P(binol) site. The P–P bond lengths in **16** are *ca.* 0.03 Å shorter than in the free ligand **1** and the unbound P^iPr_2 groups adopt an *anti* conformation about the $P_2Mo(CO)_2$ plane (approximately C_2 symmetry). The ^{31}P NMR spectrum of **16** shows two apparent doublets of triplets (see SI for the spectrum) which is due to a deceptively simple pattern for the AA'XX' spin system.

In addition to the stereoelectronic arguments that were used above to explain the nature of the borane adducts (where only σ-bonding is involved), in the case of the Mo(0) complex, a significant π-component to the P–Mo bond would be expected and this would favour binding at the P(binol) site. The ν_{CO} value for **16** of 2032 cm^{-1} is similar to the values reported for *cis*-$[Mo\{PMe(OMe)_2\}_2(CO)_4]$ (2032 cm^{-1})[34] and *cis*-$[Mo\{(MeO)_2PCH_2CH_2P(OMe)_2\}(CO)_4]$ (2033 cm^{-1})[35] which is consistent with **1** having σ-donor/π-acceptor ligand binding properties akin to a phosphonite.

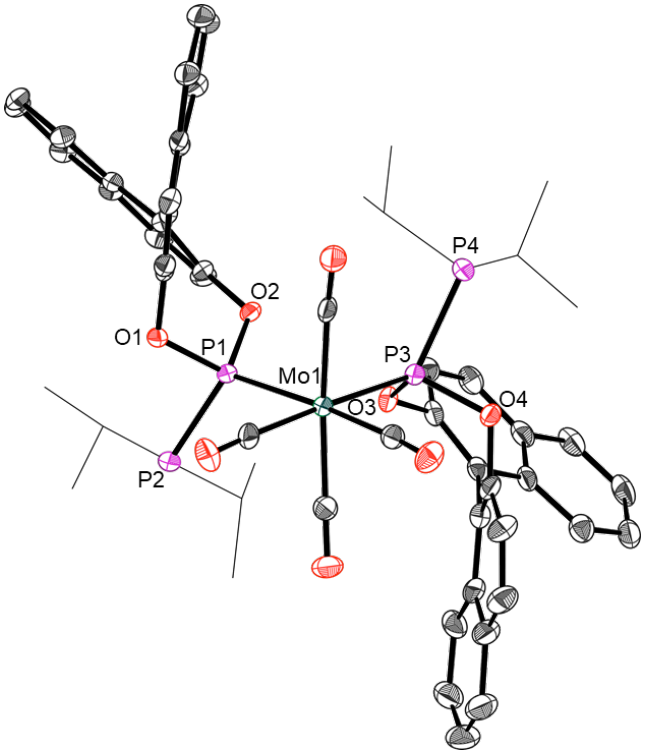


Figure 2. X-ray crystal structure of **16** Selected bond lengths (Å) and angles (°) for **16**: Mo1-P1 2.4798(9), Mo1-P3 2.4836(9), P1-P2 2.2061(12), P3-P4 2.2085(12), P1-Mo1-P3 92.50(3), O1-P1-P2 94.76(9), O2-P1-P2 114.70(9) , O1-P1-O2 100.69(12), O3-P3-P4 115.32(10), O4-P3-P4 93.16(9), O3-P3-O4 101.42(12).

Conclusions

Phosphophosphidites derived from optically active 1,1'-bi-2-naphthol are efficiently produced from a chlorosilane elimination reaction between R_2PSiMe_3 and (binol)PCl which opens up these P-analogues of the ubiquitous phosphoramidites to further study. The chemistry revealed here and summarised in Scheme 2 can be divided into reactions that involve P–P bond cleavage and those that involve P–P bond retention in the same way that can be done for $Ph_2P–PPh_2$ (Scheme 1).

The P–P bond in **1** is readily cleaved by ROH (R = H, Me, Mesityl) to give the secondary phosphine R_2PH and (binol)POR; this high kinetic lability compared to other diphosphanes is

likely a reflection of the highly polar nature of the P–P bond in **1**. In this respect, the phosphophosphidite **1** differs sharply from its air-stable phosphoramidite analogue **A**, consonant with the P–N bond being much stronger than the P–P bond.

Di-isopropylamine did not react at all with **1** under ambient conditions and pyrrollidine reacted only very slowly with **1** to give the products of sequential P–O cleavages; this represents a rare example of substitution reactions of a diphosphane occurring at a P centre.[3,18] The differences in the kinetics and the sites of the protonolysis observed in the reactions of **1** with ROH and R_2NH may be rationalised in terms of the greater Brønsted acidity and lower steric bulk of ROH than R_2NH.

The lone pairs on the P-atoms in **1** have different donor capacities and it might be predicted that the P^iPr_2, being the more electron rich, would be the preferred site for Lewis acids and transition metals to bind. However, this prediction does not take account of the lower steric hindrance to binding at the $P(binol)_2$ site and the greater π-acceptor capacity of the $P(OR)_2$ which would favour its binding to electron rich, low oxidation state metals. This balance of factors can be used to rationalise why the ^{31}P NMR evidence shows that reaction of **1** with $BH_3.SMe_2$ produces Lewis adducts in which BH_3 binds to both P-sites with essentially equal affinity and coordination to Mo(0) gave exclusively coordination at the $P(OR)_2$ site.

The ready availability of phosphophosphidites such as **1-5** will allow further development of the stoichiometric chemistry of this class of diphosphanes. However, the high reactivity of **1** to protic compounds, including traces of water, probably makes it impractical for applications of phosphophosphidites such as **1** in catalysis.

Experimental Section

General Procedures: Unless otherwise stated, all manipulations were performed under an atmosphere of dry nitrogen or argon using standard Schlenk line and glove-box techniques and oven dried (200 °C) glassware. Solvents used were collected anhydrous from a Grubbs-type solvent purification system and were degassed by repeated freeze-pump-thaw cycles. Deuterated solvents (CD_2Cl_2 and C_6D_6) and $[Mo(CO)_4(nbd)]$ were each purchased from

Sigma Aldrich and dried over CaH_2 overnight at ambient temperature followed by vacuum distillation. All solvents were stored over 4 Å molecular sieves (3 Å in the case of acetonitrile) which had been activated beforehand, 10^{-2} Torr at 200 °C for 24 h. Silylphosphines and phosphochloridite (*S*-binol)P–Cl were prepared according to reported methods.[1,2] NMR spectra were acquired at ambient temperature using Jeol ECP (Eclipse) 300, Jeol ECS 300 and Jeol ECS 400 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent peaks. ^{11}B and ^{31}P NMR spectra were referenced to $BF_3{\cdot}OEt_2$ and 85% H_3PO_4 respectively. Mass Spectrometry was performed by the Mass Spectrometry Service at the University of Bristol on either a VG Analytical Autospec (EI) or VG Analytical Quattro (ESI) spectrometer. X-ray crystallography was performed by the University of Bristol X-ray Analytical Service using a Bruker Kappa Apex II diffractometer.

Synthesis of phosphophosphidite 1: A solution of *i*Pr$_2$PSiMe$_3$ (128 mg, 0.314 mmol) in CH_2Cl_2 (1.0 ml) was added to a solution of (*S*)-BinolPCl (200 mg, 0.285 mmol) in CH_2Cl_2 (3.0 ml) and the resulting solution was stirred at ambient temperature for 1 h. The solvent and $ClSiMe_3$ were removed *in vacuo* to give a sticky solid which was then dissolved in toluene (10 ml) to give a cloudy solution which was filtered through silica. The silica was washed with toluene (10 ml) and then the toluene was removed *in vacuo* from the combined extracts to give a clear viscous oil. This oil was dissolved in hexane (5 ml) followed by removal of the solvent under reduced pressure to give a white sticky solid, (131 mg, 53%). Crystals of **1** were obtained by heating a sample of the product under vacuum at 100 °C and allowing the resultant oil to solidify at ambient temperature over a period of 14 days. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz) (δ, ppm): 260.1 (d, $^{1}J_{PP}$ = 267 Hz), -0.5 (d, $^{1}J_{PP}$ = 267 Hz). ^{1}H NMR (C_6D_6, 400 MHz) (δ, ppm): 7.68 (d, 1H, $^{3}J_{HH}$ = 8.8 Hz, Ar-C*H*), 7.62 (app. t, 3H, $^{3}J_{HH}$ = 9.0 Hz, Ar-C*H*), 7.54 (dd, 1H, *J* = 8.8 Hz, *J* = 1.4 Hz, Ar-C*H*), 7.46 (m, 2H, Ar-C*H*), 7.41 (dd, 1H, *J* = 8.8 Hz, *J* = 0.8 Hz, Ar-C*H*), 7.11 (m, 2H, Ar -C*H*), 6.91 (m, 2H, Ar -C*H*), 2.31 (dsd, 1H, *J* = 7.0 Hz, *J* = 7.0 Hz, *J* = 2.7 Hz, *i*Pr-C*H*), 2.12 (sdd, 1H, *J* = 7.2 Hz, *J* = 3.7 Hz, *J* = 1.3 Hz, *i*Pr-C*H*), 1.38 (dd, 3H, $^{3}J_{HP}$ = 11.9 Hz, $^{3}J_{HH}$ = 7.0 Hz, *i*Pr-CH_3), 1.21 (dd, 3H, $^{3}J_{HP}$ = 12.9 Hz, $^{3}J_{HH}$ = 7.1 Hz, *i*Pr-CH_3), 1.08 (dd, 3H, $^{3}J_{HP}$ = 11.8 Hz, $^{3}J_{HH}$ = 7.2 Hz, *i*Pr-CH_3), 0.99 (dd, 3H, $^{3}J_{HP}$ = 12.8 Hz, $^{3}J_{HH}$ = 7.2 Hz, *i*Pr-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 101 MHz) (δ, ppm): 151.8 (dd, *J* =

4.1 Hz, *J* = 1.5 Hz, quat. *C*), 151.5 (dd, *J* = 6.3 Hz, *J* = 2.3 Hz, quat. *C*), 133.6 (d, *J* = 1.6 Hz, quat. *C*), 133.3 (d, *J* = 1.1 Hz, quat. *C*), 132.2 (d, *J* = 1.1 Hz, quat. *C*), 131.7 (s, quat. *C*), 131.2 (d, *J* = 0.9 Hz, Ar-*C*H), 129.9 (s, Ar-*C*H), 128.7 (s, Ar-*C*H), 128.7 (s, Ar-*C*H), 127.5 (s, Ar-*C*H), 127.3 (s, Ar-*C*H), 126.7 (s, Ar-*C*H), 126.5 (s, Ar-*C*H), 125.6 (d, *J* = 5.7 Hz, quat. *C*), 125.3 (s, Ar-*C*H), 125.1 (s, Ar-*C*H), 124.2 (d, *J* = 2.7 Hz, quat.-*C*), 123.3 (d, *J* = 2.5 Hz, Ar-*C*H), 121.6 (d, *J* = 1.4 Hz, Ar-*C*H), 22.8 (dd, *J* = 23.3 Hz, *J* = 4.3 Hz, *i*Pr-*C*H), 21.9 (d, *J* = 7.3 Hz, *i*Pr-*C*H_3) 21.7-21.2 (m, *i*Pr-*C*H + 2 x *i*Pr-*C*H_3), 21.0 (dd, *J* = 10.1 Hz, 3.1 Hz, *i*Pr-*C*H_3). HR-MS (ESI): *m/z* calculated for $C_{26}H_{27}O_2P_2$ $[M + H]^{\bullet+}$ = 433.1481, obs. = 433.1470.

Synthesis of phosphophosphidite 2: A solution of Cy_2PSiMe_3 (154 mg, 0.570 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of (*S*)-BinolPCl (200 mg, 0.570 mmol) in CH_2Cl_2 (1.5 ml) and the resulting solution was stirred at ambient temperature for 30 min. The volatiles were removed *in vacuo* to give a white solid, (280 mg, 96%). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz) (δ, ppm): 262.0 (d, *J* = 261 Hz), -8.9 (d, *J* = 261 Hz). ^1H NMR (C_6D_6, 400 MHz) (δ, ppm): 8.04 (d, 1H, *J* = 8.8 Hz, Ar-C*H*), 7.95 (m, 3H, Ar-C*H*), 7.51 (dd, 1H, *J* = 8.8 Hz, *J* = 0.8 Hz, Ar-C*H*), 7.43 (m, 3H, Ar-C*H*), 7.28 (m, 4H, Ar-C*H*), 2.28 (m, 1H, Cy-C*H*), 2.09 (br. s, 1H, Cy-C*H*), 1.97 (m, 2H, Cy-CH_2), 1.86-1.58 (br. m, 9H, Cy-CH_2), 1.49-1.11 (m, 9H, Cy-CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz) (δ, ppm): 133.4 (s, quat. *C*), 133.2 (s, quat. *C*), 132.2 (s, Ar-*C*H), 131.7 (s, Ar-*C*H), 131.3 (s, Ar-*C*H), 130.0 (s, Ar-*C*H), 129.1 (s, Ar-*C*H), 129.0 (s, Ar-*C*H), 128.9 (s, Ar-*C*H), 127.2 (s, Ar-*C*H), 126.8 (s, Ar-*C*H), 126.6 (s, Ar-*C*H), 125.6 (s, Ar-*C*H), 125.4 (s, Ar-*C*H), 123.3 (d, J_{CP} = 2.2 Hz, Ar-*C*H), 121.8 (s, Ar-*C*H), 33.0 (dd, J_{CP} = 22.2 Hz, J_{CP} = 4.8 Hz, Cy-*C*H), 32.4 (dd, J_{CP} = 11.9 Hz, J_{CP} = 7.0 Hz, Cy-*C*H_2), 31.4 (m, Cy-*C*H), 30.2 (m, Cy-C*H*), 28.3 (dd, J_{CP} = 13.7 Hz, J_{CP} = 9.3 Hz, Cy-*C*H_2), 27.9 (app. t, J_{CP} = 8.8 Hz, Cy-*C*H_2), 26.9 (s, Cy-*C*H_2), 26.8 (s, Cy-*C*H_2).

Synthesis of phosphophosphidite 3: A solution of *t*-Bu_2PSiMe_3 (327 mg, 1.50 mmol) in CH_2Cl_2 (3.0 ml) was added to a solution of (*S*)-BinolPCl (500 mg, 1.53 mmol) in CH_2Cl_2 (3.0 ml) and the resulting solution was stirred at ambient temperature for 45 min. The solvent and $ClSiMe_3$ were removed *in vacuo* to give a sticky white solid which was dissolved in toluene (10 ml) and filtered through celite, which was then washed with toluene (10 ml). The toluene

was removed *in vacuo* to give a sticky white solid, which was dissolved in hexane (5 ml) followed by removal under reduced pressure to give a white solid, (310 mg, 47%). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz) (δ, ppm): 260.6 (d, $^{1}J_{PP}$ = 285 Hz), 26.0 (d, $^{1}J_{PP}$ = 285 Hz). ^{1}H NMR (C_6D_6, 400 MHz) (δ, ppm): 7.70 (d, 1H, $^{3}J_{HH}$ = 8.8 Hz, Ar-C*H*), 7.61 (m, 4H, Ar-C*H*), 7.48 (m, 2H, Ar-C*H*), 7.40 (dd, 1H, *J* = 8.8 Hz, *J* = 0.8 Hz, Ar-C*H*), 7.11 (m, 2H, Ar-C*H*), 6.92 (m, 2H, Ar-C*H*), 1.47 (d, 9H, $^{3}J_{HP}$ = 10.5 Hz, *t*Bu-CH_3), 1.20 (d, 9H, $^{3}J_{HP}$ = 11.4 Hz, *t*Bu-CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 101 MHz) (δ, ppm): 151.7 (d, *J* = 3.8 Hz, quat. *C*), 151.4 (dd, *J* = 6.9 Hz, *J* = 2.3 Hz, quat. *C*), 133.6 (d, *J* = 1.8 Hz, quat. *C*), 133.2 (d, *J* = 1.1 Hz, quat. *C*), 132.2 (d, *J* = 1.0 Hz, quat. *C*), 131.6 (s, quat. *C*), 131.1 (d, *J* = 0.8 Hz, Ar-*C*H), 129.6 (s, Ar-*C*H), 128.7 (s, Ar-*C*H), 128.6 (s, Ar-*C*H), 127.5 (s, Ar-*C*H), 127.3 (s, Ar-*C*H), 126.7 (s, Ar-*C*H), 126.4 (s, Ar-*C*H), 125.8 (d, *J* = 5.5 Hz, quat.*C*), 125.3 (s, Ar-*C*H), 125.0 (s, Ar-*C*H), 124.1 (d, *J* = 2.7 Hz, quat. *C*), 124.0 (d, *J* = 3.0 Hz, Ar-*C*H), 121.6 (d, *J* = 1.6 Hz, Ar-*C*H), 31.7 (dd, *J* = 23.8 Hz, *J* = 12.1 Hz, *t*Bu-*C*CH_3), quaternary *t*Bu-*C* atoms were not observed. HR-MS (ESI): *m/z* calculated for the monoxide of the assigned product $C_{28}H_{31}O_3P_2$ $[MO + H]^{\bullet+}$ = 477.1748, obs. = 477.1736. The CD spectrum of **3** in thf has been measured and has a form related to that of *S*-binol (see SI for the spectra).

Synthesis of phosphophosphidite 4: A solution of *s*-PhobPSiMe$_3$ (134 mg, 0.627 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of (*S*)-BinolPCl (200 mg, 0.570 mmol) in CH_2Cl_2 (1.5 ml) and the resulting solution was stirred at ambient temperature for 30 min. The volatiles were removed *in vacuo* to give a white solid, (240 mg, 92%). **$^{31}P\{^{1}H\}$ NMR** (C_6D_6, 162 MHz) (δ, ppm): 257.2 (d, $^{1}J_{PP}$ = 258 Hz), -32.8 (d, $^{1}J_{PP}$ = 258 Hz). ^{1}H NMR (C_6D_6, 400 MHz) (δ, ppm): 7.69-7.60 (m, 4H, Ar-C*H*), 7.50-7.43 (m, 4H, Ar-C*H*), 7.14-7.09 (m, 2H, Ar-C*H*), 6.95-6.88 (m, 2H, Ar-C*H*), 2.89 (m, 1H, Phob-CH_2), 2.71 (m, 1H, Phob-C H_2), 2.26 (br. s, 1H, Phob-C*H*), 2.11 (br. s, 1H, Phob-C*H*), 2.01 (m, 2H, Phob-CH_2), 1.91-1.71 (m, 8H, Phob-CH_2). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 101 MHz) (δ, ppm): 152.1 (dd, J_{CP} = 3.9 Hz, J_{CP} = 2.7 Hz, quat. *C*), 151.5 (dd, J_{CP} = 5.6 Hz, J_{CP} = 3.4 Hz, quat. *C*), 133.7 (d, J_{CP} = 1.6 Hz, quat. *C*) 133.5 (d, J_{CP} = 1.0 Hz, quat. *C*), 132.2 (d, J_{CP} = 0.8 Hz, quat. *C*), 131.7 (s, quat. *C*), 131.2 (s, Ar-*C*H), 129.8 (s, Ar-*C*H), 128.7 (s, Ar-*C*H), 128.7 (s, Ar-*C*H), 127.5 (s, Ar-*C*H), 127.4 (s, Ar-*C*H), 126.7 (s, Ar-*C*H), 126.5 (s, Ar-*C*H), 125.8 (d, J_{CP} = 5.9 Hz, quat. *C*), 125.2 (s, Ar-

*C*H), 125.0 (s, Ar-*C*H), 124.0 (d, J_{CP} = 2.7 Hz, quat. *C*), 123.5 (d, J_{CP} = 3.8 Hz, Ar-*C*H), 121.7 (s, Ar-*C*H), 32.7 (m, Phob.-*C*H_2), 29.3 (m, Phob.-*C*H_2), 25.2 (dd, J_{CP} = 18.9 Hz, J_{CP} = 1.3 Hz, Phob.-*C*H), 24.3 (dd, J_{CP} = 14.8 Hz, J_{CP} = 8.2 Hz, Phob.-*C*H), 23.0 (m, Phob.-*C*H_2). HR-MS (ESI): *m/z* calculated for the monoxide of the assigned product $C_{28}H_{27}O_3P_2$ [MO + H]$^{\bullet+}$ = 473.1435, obs. = 473.1446.

Synthesis of phosphophosphidite 5: A solution of Ph_2PSiMe_3 (369 mg, 1.43 mmol) in CH_2Cl_2 (5.0 ml) was added to a solution of (*S*)-BinolPCl (500 mg, 1.43 mmol) in CH_2Cl_2 (5.0 ml) and the solution was stirred for 30 min. After this time, ^{31}P NMR spectroscopy revealed that the starting materials had been consumed and the product **5** was present in approximately 90% purity with two by-products each making up up 5% of the P-containing species. The volatiles were removed *in vacuo* to give an off-white solid. $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz) (δ, ppm): 230.2 (d, $^1J_{PP}$ = 228 Hz) -21.3 (d, $^1J_{PP}$ = 228 Hz); -14.3 (s, 5%, Ph_2P–PPh_2); 209.6 (s, 5%, P_2(binol)$_4$). ^{1}H NMR (C_6D_6, 400 MHz) (δ, ppm). The spectrum confirmed the presence of a mixture of products was formed by the series of overlapping signals in the aromatic C–H region that were observed: 7.87 (m, 2H), 7.63 (m, 2H), 7.56 (m, 3H), 7.49-7.32 (m, 4H), 7.18-7.08 (m, 6H), 7.03 (m, 2H), 6.97-6.87 (m, 3H). HR-MS (ESI): *m/z* calculated for monoxide of **5** $C_{32}H_{23}O_3P_2$ [MO + H] = 517.1122, obs. = 517.1126; *m/z* calculated for Ph_2P–PPh_2; [M + H] = 371.1118, obs. = 371.1117. *m/z* calculated for monoxide of P_2(binol)$_4$ [MO + H]$^+$ = 647.1177, obs. = 647.1172.

NMR studies of the reactions of 1: *(1) Reaction of **1** with water:* A 0.278 M solution of H_2O in THF (0.20 mL, 0.055 mmol) was added to a solution of **1** (24 mg, 0.055 mmol) in THF (0.4 mL) in an NMR tube. The reaction was monitored by ^{31}P NMR spectroscopy and after 20 min at ambient temperature, it was observed that all of the **1** had been consumed and new ^{31}P NMR signals were observed corresponding to BinolP(O)H and HP^{i}Pr$_2$. ^{31}P NMR (THF, 121 MHz) (δ, ppm): 14.5 (d, J_{PH} = 737 Hz, Binol*P*(O)H), -15.5 (br. d, J_{PH} = 164 Hz, H*P*^{i}Pr$_2$). The volatiles were removed under vacuum to give a white solid which was dissolved in C_6D_6. ^{31}P NMR (C_6D_6, 162 MHz) (δ, ppm): 13.8 (d, J_{PH} = 727 Hz, Binol*P*(O)H). ^{1}H NMR (C_6D_6, 400 MHz) (δ, ppm): 7.50 (m, 5H, Ar-C*H*), 7.30 (m, 2H, Ar-C*H*), 7.10 (m, 2H, Ar-C*H*), 6.94

(dd, 1H, J = 8.8 Hz, J = 1.2 Hz, Ar-C*H*), 6.87 (m, 2H, Ar-C*H*), 6.81 (d, 1H, J_{PH} = 727 Hz, P(O)*H*) (see Fig. S1-S3)

*(2) Reaction of **1** with methanol:* A 0.077 M solution of MeOH in THF (0.30 mL, 0.023 mmol) was added to **1** (10 mg, 0.023 mmol) in an NMR tube and the reaction was monitored by ^{31}P NMR spectroscopy. After 23 h at ambient temperature, the ^{31}P NMR spectrum showed that >90% of **1** had been consumed and there were two new ^{31}P NMR signals at +138 ppm (q, $^{2}J_{PH}$ = 9 Hz) and -16 ppm (br. d, $^{1}J_{PH}$ = 192 Hz) which correspond to the phosphite **7**[29] and HP^{i}Pr$_2$ respectively (see Figure S5).

*(3) Reaction of **1** with mesitol:* A solution of mesitol (4.7 mg, 0.035 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of **1** (15 mg, 0.035 mmol) CD_2Cl_2 (0.3 mL), the solution was transferred to a J. Young NMR tube and the reaction was monitored by ^{31}P NMR spectroscopy. After 17 d at ambient temperature, the ^{31}P NMR spectrum showed that **1** had been consumed and there were two new ^{31}P NMR signals at +149 ppm and -16 ppm (d, $^{1}J_{PH}$ = 192 Hz) which correspond to the phosphite **8**[30] and HP^{i}Pr$_2$ respectively. Mass spectrometry analysis of the solution confirms the presence of the phosphite **8**. HR-MS (MALDI): *m/z* calculated for $C_{29}H_{23}O_3P$ $[M + H]^{\bullet+}$ = 451.1458, obs. = 451.1465.

*(4) Reaction of **1** with pyrollidine:* Compound **1** was dissolved in pyrrolidine (0.5 mL) in an NMR tube and the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. After 70 min at ambient temperature, the ^{31}P{^{1}H} NMR spectrum showed that **1** had been consumed and there were two new sets of doublets at 145.0 / -4.8 ppm (J_{PP} = 191 Hz) and +146.0 / -5.8 ppm (J = 191 Hz) which correspond to the two diastereoisomers **9** and **10** (Figure S6). After 40 h at ambient temperature, another set of doublets are apparent at +76.0 and -21.0 ppm (J_{PP} = 202 Hz) which were assigned to the P–P bonded species **11** (Figure S7). Also observed were two minor signals at -16 and +103 ppm which are assigned to HP^{i}Pr$_2$ and tris(pyrrolidino)phosphine respectively.[31]

Synthesis of bis(borane) adduct 13: A solution of $H_3B{\cdot}SMe_2$ (7.0 mg, 0.092 mmol) in CH_2Cl_2 (0.3 ml) was added to a solution of **1** (20 mg, 0.046 mmol) in CH_2Cl_2 (0.3 ml) and

transferred to a J Young NMR tube. The solution was kept at ambient temperature for 30 min and then the volatiles were removed under reduced pressure to give a white solid, (20 mg, 94%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz) (δ, ppm): 181.8 (br. d, J = 210 Hz), 47.6 (d, J = 210 Hz). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2, 128 MHz) (δ, ppm): -38.9 (br. s, 1B), -44.1 (br. s, 1B). ^{1}H NMR (CD_2Cl_2, 400 MHz) (δ, ppm): 8.07 (dd, 2H, J = 17.8 Hz, J = 9.0 Hz, Ar-C*H*), 8.00 (t, 2H, J = 7.7 Hz, Ar-C*H*), 7.64 (dd, 1H, J = 8.9 Hz, 1.0 Hz, ArC*H*), 7.51 (m, 3H, ArC*H*), 7.28 (m, 3H, ArC*H*), 7.18 (d, 1H, J = 8.6 Hz, Ar-C*H*), 2.72 (ddsept, 1H, J = 14.3 Hz, J = 11.0 Hz, J = 7.2 Hz, iPr-C*H*), 2.72 (dtt, 1 H, J = 14.3 Hz, J = 9.5 Hz, J = 7.2 Hz, iPr-C*H*), 1.4 (dd, 3H, J = 15.5 Hz, J = 7.1 Hz, iPr-CH_3), 1.40 (dd, 3H, J = 16.2 Hz, J = 7.1 Hz, iPr-CH_3), 1.30 (dd, 3H, J = 15.7 Hz, J = 7.1 Hz, iPr-CH_3), 1.25 (dd, 3H, J = 15.8 Hz, J = 7.2 Hz, iPr-CH_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 101 MHz) (δ, ppm): 149.3 (d, J = 13.3 Hz, quat. *C*), 147.6 (dd, J = 8.8 Hz, J = 1.8 Hz, quat. *C*), 133.0 (d, J = 1.3 Hz, quat. *C*), 132.8 (s, quat. *C*), 132.3 (s, quat. *C*), 131.6 (s,f Ar-*C*H), 131.2 (s, Ar-*C*H), 129.1 (d, J = 18.9 Hz, Ar-*C*H), 127.5 (d, J = 28.6 Hz, Ar-*C*H), 127.4 (d, J = 24.0 Hz, Ar-*C*H), 126.5 (d, J = 19.6 Hz, Ar-*C*H), 123.1 (d, J = 3.4 Hz, quat.-*C*), 122.3 (d, J = 2.2 Hz, Ar-*C*H), 122.0 (d, J = 2.2 Hz, Ar-*C*H), 121.8 (d, J = 3.0 Hz, quat. *C*), 24.3 (dd, J = 19.5 Hz, J = 2.5 Hz, *i*Pr-*C*H), 23.1 (dd, J = 22.3 Hz, J = 6.3 Hz, *i*Pr-*C*H), 18.9 (d, J = 2.3 Hz, *i*Pr-*C*H_3), 18.6 (s, *i*Pr-*C*H_3), 18.1 (d, J = 2.2 Hz, *i*Pr-*C*H_3), 18.1 (d, J = 3.3 Hz, *i*Pr-*C*H_3). HR-MS (ESI): *m/z* calculated for $C_{26}H_{32}B_2NaO_2P_2$ $[M + Na]^+$ = 483.1965, obs. = 483.1950.

Synthesis of *cis*-[Mo(CO)$_4$(1)] (16): Compound **1** (20 mg, 0.046 mmol) was dissolved in CH_2Cl_2 (0.3 mL) and was added to a solution of [Mo(nbd)(CO)$_4$] (7 mg, 0.022 mmol) in CH_2Cl_2 (0.3 mL). After 18 h at ambient temperature, the solution was concentrated to 0.1 mL *in vacuo* and then hexane added to form an upper layer. The product then crystallised after 7 days (10 mg, 42%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz) (δ, ppm): 269.2 (dt, J = 285, 31 Hz), 42.7 (dt, J = 285, 31 Hz). ^{1}H NMR (CD_2Cl_2, 400 MHz) (δ, ppm): 8.06 (d, 2H, J = 8.9 Hz, ArC*H*), 7.98 (m, 6H, ArC*H*), 7.70 (d, 2H, J = 8.8 Hz, ArC*H*), 7.45 (m, 6H, ArC*H*), 7.22 (m, 6H, ArC*H*), 7.13 (d, 2H, J = 8.1 Hz, ArC*H*), 2.38 (m, 2H, iPr-C*H*), 2.29 (m, 2H, iPr-C*H*), 1.05 (dd, 6H, J = 12.0 Hz, J = 7.0 Hz, iPr-CH_3), 0.94 (dd, 6H, J = 7.2 Hz, J = 2.7 Hz, iPr-

CH_3), 0.90 (d, 6H, J = 7.2 Hz, iPr-CH_3), 0.71 (dd, 6H, J = 11.1 Hz, J = 7.0 Hz, iPr-CH_3). IR spectrum (CH_2Cl_2): 2032 cm^{-1} (ν_{CO}).

X-Ray crystallography. The details of the X-ray crystal structure determinations of **1** and **16** are given in the SI. Crystallographic data for compounds **1** and **16** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1885866-1885867. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

TOC text

The high reactivity of phosphophosphidite **1** contrasts with the inertness of its N-analogue, phosphoramidite **A**. The P-P bond in **1** is readily cleaved by water or methanol but remains intact in the Lewis adducts of **1** with BH_3 and in the complex $[Mo(CO)_4(\mathbf{1})_2]$.

Key Topics

P–P bond reactivity

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